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POLY[BIS(PHENOXY)PHOSPHAZENE]-(PBPP) CRYSTALS

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by

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Whenever solution grown $\alpha$-form (3-D) crystals of PBPP were heated in the thermotropic region between T(1) and Tm (the isotropic temperature) they convert to the 2D pseudo-hexagonal, $\delta$-form crystals. Upon rapid quenching into liquid nitrogen the $\delta$ form "frozen-in" still remains upon warming to room temperature. Further heating close to T(1) produces a 3-D hexagonal modification ($\epsilon$ form) which is a morphological modification of the monoclinic $\alpha$-form of PBPP confirmed already by electron diffraction measurements.

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# CRYSTALLIZATION RELATIONSHIPS BETWEEN
# POLY[BIS(PHENOXY)PHOSPHAZENE]-(PBPP) CRSYTALS

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## ABSTRACT

Whenever solution grown α-form (3D) crystals of PBPP were heated in the thermotropic region between T(1) and Tm (the isotropic temperature) they convert to the 2D pseudohexagonal, δ-form crystals. Upon rapid quenching into liquid nitrogen the δ form "frozen-in" still remains upon warming to room temperature. Further heating close to T(1) produces a 3-D hexagonal modification (ε-form) which is a morphological modification of the monoclinic α-form of PBPP confirmed already by electron diffraction measurements.

## INTRODUCTION

Structural and morphological investigations of semi-crystalline polyphosphazenes have been made in order to examine and to clarify the nature of the behavior through the thermotropic transition (1) - (9). Solution grown crystals have been described (1) - (8) and some crystalline modifications were elucidated (1), (3), (6), (7). PBPP crystals can be grown from xylene or cyclohexanone solvents to form monoclinic (α-form) crystals. Whenever these crystals are heated through T(1) and then cooled again to room temperature, 2D pseudohexagonal δ-form and 3D orthorhombic γ-form coexist (3). Crystallographic relationships amongst these modifications of PBPP have been established (2). Our intent in the present work has been to obtain more detailed structural and morphological information relevant to the T(1) phase transition in polyphosphazenes. This paper is concerned with the formation of morphological modifications of PBPP crystals formed from the disordered state that exists between T(1) and Tm.

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# EXPERIMENTAL

## Materials:

Chemically pure unfractionated poly[bis(phenoxy)phosphazene]-PBPP of narrow molecular weight (Mw/Mn< 3) and another sample of broader (Mw/Mn>6) molecular weight distribution was used in this study.

## Solution Grown Crystals:

Crystals were grown from 0.015 wt% PBPP in xylene solution at 65°C for 20 hr. After crystallization, the crystals were washed with fresh xylene at 65°C in order to remove or prevent potentially crystallizable low molecular weight polymer from contaminating the crystals.

## Preparations for Electron Microscopy:

(i) PBPP Crsytals supported on carbon film on microscope grids, were heated mostly at 180°C for 1 hr., but temperatures as high as 250°C, were sometimes used. All heat treatments were conducted in nitrogen, followed by quenching into liquid nitrogen. Alternatively cooling to room temperature at a rate of 2°C/min. was also used.

(ii) In other experiments crystals were heated isothermally at 100°C and 120°C respectively (ie below T(1)) and at others were maintained 150°C above T(1) for 1 hr. before being cooled down slowly to room temperature.

## Electron Microscopy:

Samples were examined with a JEOL JEM-200 CX electron microscope at 200KV. Samples were shadowed sometimes with Pd/Au (40/60) metal alloy to enhance specimen contrast.

## RESULTS AND DISCUSSION

Well-defined lathe-shaped PBPP crystals have been reported from dilute xylene solution of polymer (1). Figure 1 shows a series of electron diffraction patterns of PBPP crystals following a variety of thermal treatments. Whenever α-form crystals (Fig. 1a) are heated above T(1), their thermotropic transition temperature, a 2D pseudohexagonal disordered phase is obtained (Fig. 1b). Upon cooling this specimen slowly to room temperature for instance from 180°C, a 3D orthorhombic γ-form results (Fig.1c) (2), (3).

The electron diffraction of the δ-form quenched into liquid nitrogen from above T(1) is seen to be "frozen-in" and this disordered state even exists at room temperature (see insert in Fig. 3). Note that the glass transition of this material is 6°C (10).

Figure 2 is an electron micrograph of PBPP crystals comprised of lathe-shaped crystals obtained from xylene solution by isothermal crystallization at temperature between 50°C and 70°C. The morphology depends somewhat upon the molecular weight of PBPP (1). Crystals so produced exhibit corrugations across the lateral surface direction as seen in Fig. 2. The "corrugations" seem to be formed during crystallization (more clearly seen in Fig. 2(b)) even though we do not yet understand this morphology. Whenever PBPP crystals are heated above T(1), they thickening erratically and this process is seen to be a concomitant with surface roughening of the crystals (3,8). Following quenching into liquid nitrogen from above T(1), the same crystalline shapes as are found in the orignial α-form crystals persist, with a hint of the surface corrugation still remaining (see Fig. 3).

Both of these morphologies found for the quenched PBPP and for the untreated α-form PBPP crystals remain unaltered unless the specimens are heated above T(1). However, when quenched PBPP is heated above T(1) and cooled

subsequently to room temperature, the surface morphology changes slightly (less rough in appearance) suggesting some improvement in crystallinity perhaps, with the appearance of the accompanying corrugations. Note that corrugations are more apparent whenever an improvement in crystallinity occurs, for example after heating and slow cooling (Fig. 4), and the electron diffraction pattern shows the 3D $\gamma$-form to exist at room temperature. Figure 5(a) is an electron diffraction pattern of the quenched crystal in Fig. 4 formed after heating the sample at 120°C, below T(1) for 1 hr., followed by cooling it to room temperature. It shows a hexagonal symmetry. This result indicates that a new 3D crystal modification is formed from the pseudohexagonal 2D crystal. This pattern shown in Fig. 5(a) may be indexed based upon the $\alpha$-form unit cell of the PBPP crystal. The results are listed in Table 1 and are also represented diagramatically in Fig. 5(b).

Below T(1) the $\alpha$-form remains upon heat treatment. Whenever transformation occurs from the $\alpha$-form to the $\delta$-form via T(1) transition temperature, the following crystallographic relationships between both modifications persist: namely the $[320]_\alpha$ and the $[110]_\alpha$ directions remain parallel to the $[120]_\delta$ and the $[100]_\delta$ directions respectively (2).

It has been reported that there are two molecular chains per unit cell and the chain direction lies almost directly along the [110] direction for the orthorhombic poly[di-(3,4-dimethylphenoxy)phosphazene]-PDMP crystal(11). PBPP is supposed to take on similar structural characteristics as PDMP, involving two molecular chains with four monomer units per cell respectively, the chains being located at the corners and at the center of the monoclinic unit cell. When the $\alpha$- crystals transform into the $\delta$-form molecular chains may "translate" within the $(110)_\alpha$ plane, during the disordering transformation process. The axial relationship between unit cells of the $\alpha$- and the $\delta$-form crystals is illustrated in Fig. 6 along

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with the superposed locations of the molecular chains in both of these crystal forms of PBPP. The inter-chain separation is 11.2Å in the 2D hexagonal modification (2). It is important to note that the d-spacing of $(100)_\delta$ plane, 11.2Å, coincides with that of $(110)_\alpha$ in the $\alpha$-form crystal. During the $\alpha \rightarrow \gamma$ transformation it appears that the 11.2Å, d-spacing common to both forms, is maintained in the $[110]_\alpha$ or $[100]_\delta$ direction of the monoclinic or 2D hexagonal modification. These conclusions were established from electron diffraction patterns taken from the same portion of PBPP crystals before and after the transformation (2). These relationships between the $\alpha$- and the $\delta$-forms provide an explanation for the hexagonal symmetry noted in electron diffraction pattern of Fig. 5.

We presume that the 2D hexgaonal modification, obtained by quenching from above T(1), crystallizes to the 3D $\alpha$-form modification under the proper heat treatment conditions. Molecular chains in the "disordered" states presumably "translate" within the $\{100\}_\delta$ planes but maintain the inter-chain separation at 11.2Å. On the other hand, whenever PBPP crystallizes as the monoclinic $\alpha$-form from solution, the molecular chains must grow along the $[\overline{3}20]$ direction which is the long axis direction of these lathe-shaped crystals, and chain folding must occur predominately within the (110) plane (2). Consequently, when molecular chains reorganize from the disordered hexagonal state into the monoclinic $\alpha$-form they may move along the $\{100\}_\delta$ planes in a reverse fashion to that which happens whenever the $\alpha \rightarrow \delta$ phase transition occurs. The $\delta$- hexatic phase of PBPP seen in Fig. 3 (insert) processes six equivalent (100) planes. Reorganization of the molecular chains in the $\delta$-form simultaneously occurs via advancement along the six $\{100\}_\delta$ planes. These $\{100\}_\delta$ planes also correspond to $\{110\}_\alpha$ planes as already outlined, thus it seems likely that the chains rearrange to make the $\alpha$-form

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modification. Figure 7 shows how the axial relationship of two α-form crystals may originate from the $(100)_\delta$ and the $(\bar{1}20)_\delta$ planes respectively using the reciprocal unit cell illustration of the α-forms. Each $[110]_\alpha$ direction makes an angle of 60°. In fact, all (hko) and/or $(\bar{h}ko)$ reflections except $(1\bar{1}0)$ and $(3\bar{1}0)$ reflections which are located very close to the a* axis in the a*b* reciprocal net are observed in Fig. 5(b) and spacings are given in Table 1. This behavior may also be interpreted to mean that orientational growth occurs in the $<110>_\alpha$ directions corresponding to the six $<100>_\delta$ directions of the hexagonal form of PBPP. Thus the formation of the hexagonally symmetrical pattern of Fig. 5(a) can be explained. It therefore seems that this peculiar pattern does exist as a new morphological modification of the α-form PBPP crystal specified here as the ε-form. Note that the ε-form can be obtained from the δ-form PBPP only whenever the latter is warmed to just below T(1), ie. when the system is thermally activated. The δ-form that exists between T(1) and Tm does not give rise the ε-form directly upon cooling. Only the kinetically favored and more stable γ-form is obtained directly upon cooling the δ-form specimen below T(1).

## CONCLUSION

1.  The 2D PBPP modification ($\delta$-form) exists at room temperature whenever it is quenched from abov$\cdot$ T(1) to liquid nitrogen temperature and then warmed up to room temperature.

2.  The 3D $\varepsilon$-crystal modification persists after heating the $\delta$-modification to just below T(1) followed by cooling down to room temperature.

3.  Electron diffraction patterns obtained from the heated $\delta$ form PBPP slightly below T(1) exhibits hexagonal symmetry. All reflections have been indexed using $\alpha$-form unit cell of the PBPP crystal.

4.  The hexagonal 3D $\varepsilon$-crystals appear to be a morphological modification of the well known $\alpha$-form of PBPP.

5.  The $\varepsilon$-form can be obtained only by annealing the quenched $\delta$-form PBPP just below, but close to T(1).

6.  Normal and slow cooling of the $\delta$-form from above T(1) to room temperature and below it, gives the 3D $\delta$-form of PBPP.

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## Acknowledgements

## FIGURE LEGENDS

Figure 1    Electron diffraction patterns of solution grown PBPP crystals showing
the effect of thermal history on morphology in (a) as-crystallized, at
room temperature ($\alpha$-form), (b) at 180°C ($\delta$-form), (c) after slow cooling
from 180°C to room temperature ($\gamma$-form).

Figure 2    Transmission (a) and scanning (b) electron micrograph of PBPP crystals
formed from xylene solution.

Figure 3    Room temperature electron micrograph of PBPP crystals after
quenching into liquid nitrogen from 180°C. Note the electron
diffraction insert obtained at room temperature.

Figure 4    Electron micrograph of PBPP crystals obtained after quenching from
180°C into liquid nitrogen followed by heating to 120°C for 1 hr., and
afterwards cooling to room temperature.

Figure 5    (a) Electron diffraction pattern of PBPP crystals in Fig. 4 and (b)
schematic representation of (a) with indexed reflections.

Figure 6    Relationship between the $\alpha$-form (•) and the $\delta$-form (o) PBPP showing
crystallographic axes.

Figure 7    Relationship between the two $\alpha$- forms ascribed as orginating from
the {100} planes of the $\delta$-form PBPP shown using the reciprocal unit
cell.

## TABLES

Table 1    Calculated d-spacings with Miller indices for the $\alpha$-form of PBPP and
observed d-spacings for the hexagonally symmetric reflections shown in
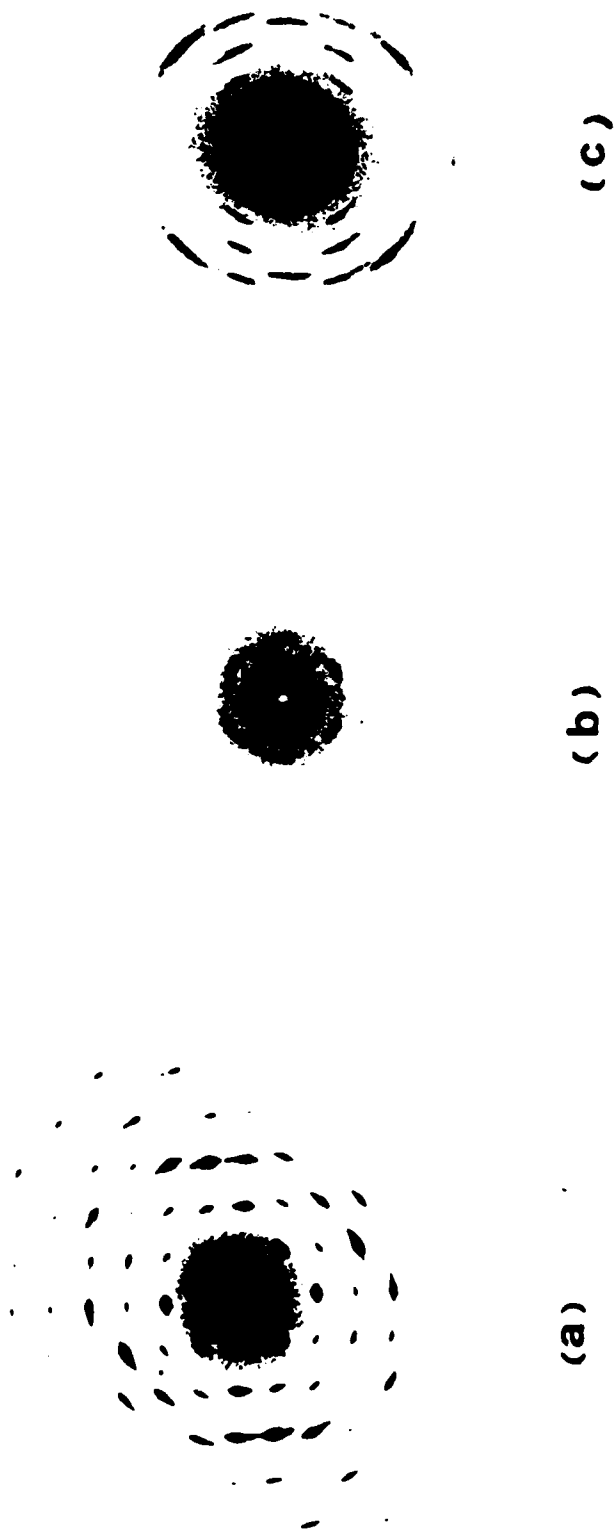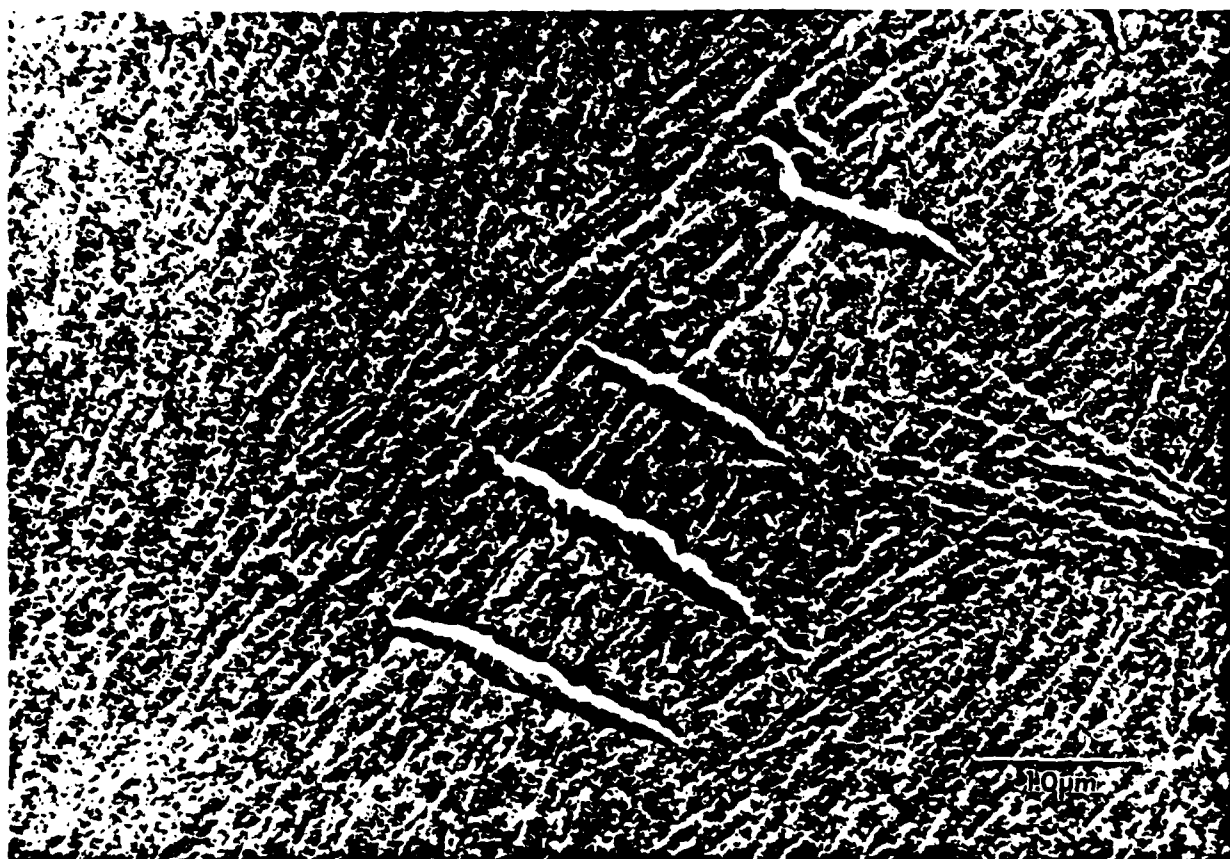Figure 5.

**(a)**

**(b)**

**(c)**

Figure 1    Electron diffraction patterns of solution grown PBPP crystals showing the effect of thermal history on morphology in (a) as-crystallized, at room temperature (α-form), (b) at 180°C (δ-form), (c) after slow cooling from 180°C to room temperature (γ-form).

(a)



(b)

Figure 2    Transmission (a) and scanning (b) electron micrograph of PBPP crystals formed from xylene solution.
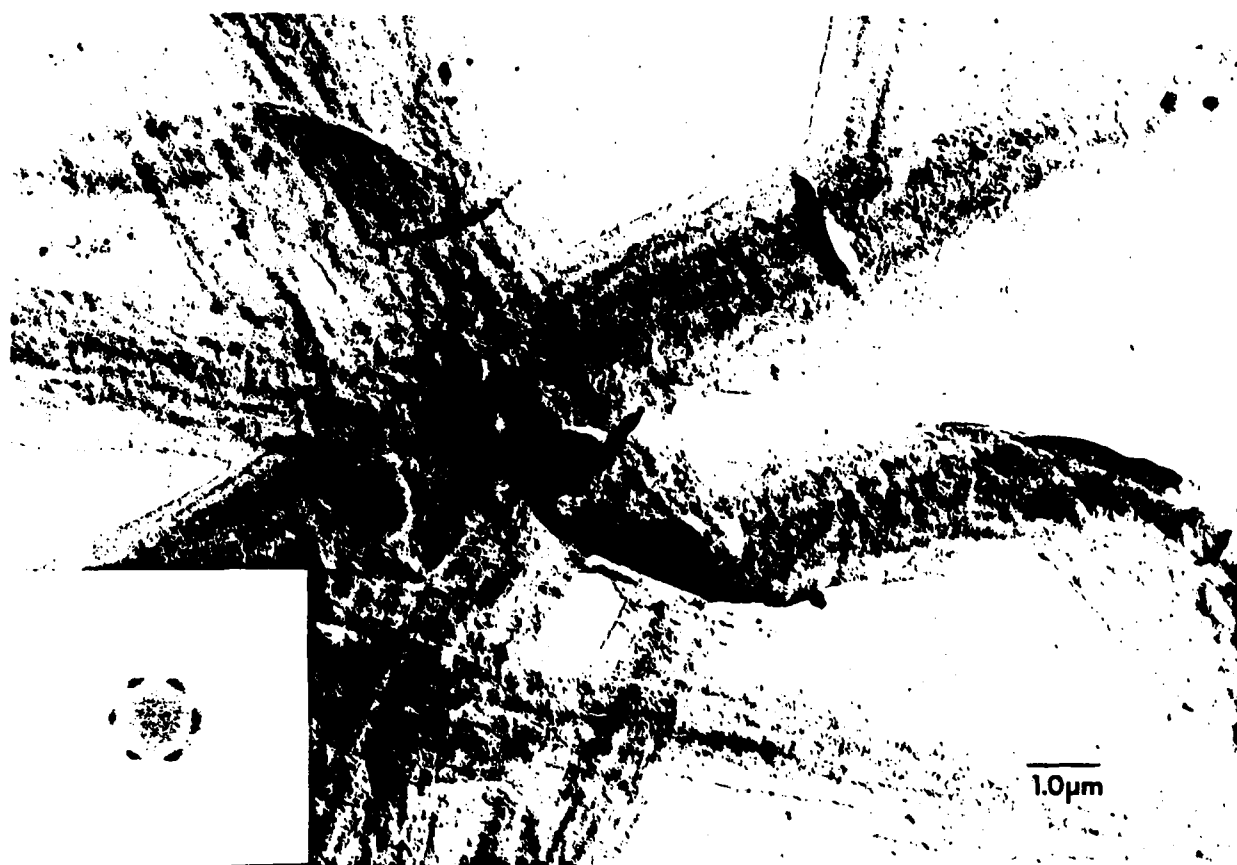
Figure 3    Room temperature electron micrograph of PBPP crystals after quenching into liquid nitrogen from 180°C. Note the electron diffraction insert obtained at room temperature.
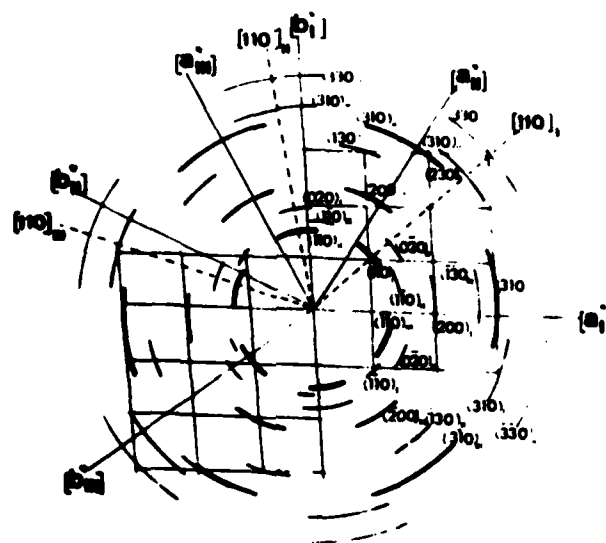
Figure 4     Electron micrograph of PBPP crystals obtained after quenching from 180°C into liquid nitrogen followed by heating to 120°C for 1 hr., and afterwards cooling to room temperature.
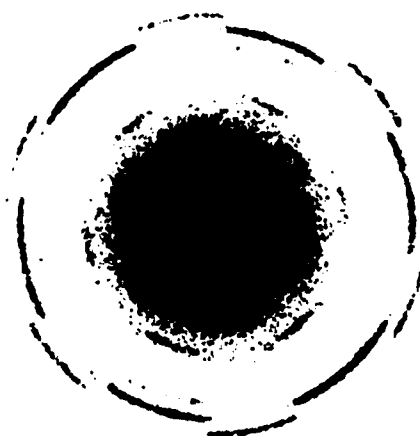
( a )

Figure 5   (a) Electron diffraction pattern of PBPP crystals in Fig. 4 and (b schematic representation of (a) with indexed reflections.

( b )

Figure 5    (a) Electron diffraction pattern of PBPP crystals in Fig. 4 and (b schematic representation of (a) with indexed reflections.
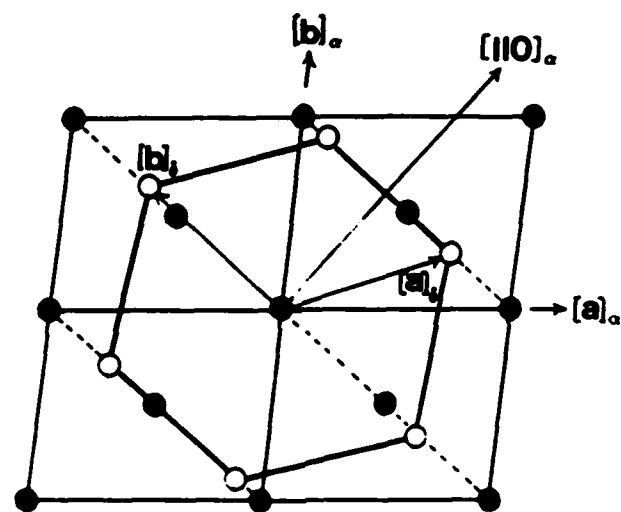
Figure 6     Relationship between the α-form (•) and the δ-form (o) PBPP showing
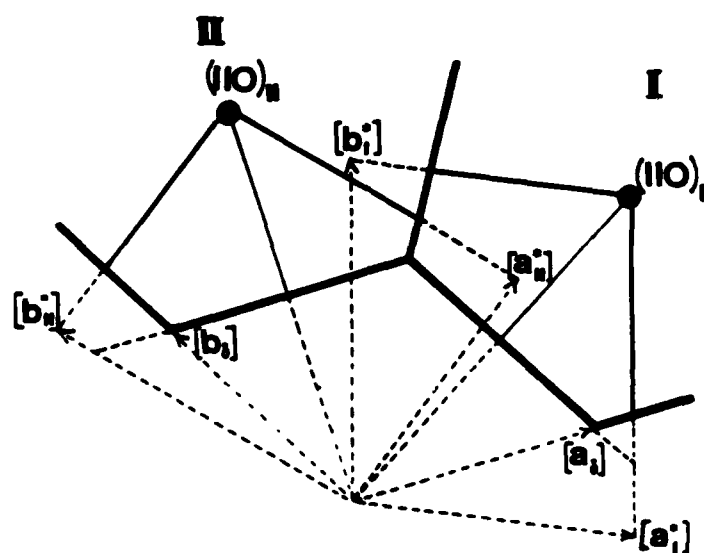crystallographic axes.

Figure 7     Relationship between the two α- forms ascribed as orginating from the (100) planes of the δ-form PBPP shown using the reciprocal unit cell

Table 1    Calculated d-spacing with Miller indices for the α-form of PBPP and observed d-spacings (A[15]) for the hexagonally symmetric reflections shown in Figure 5.

| α -Form | | | ObS. | |
| a = 16.5    b = 13.7 | | | | |
| (h k l) | d | I | d | I |
|---|---|---|---|---|
| 1 1 0 | 11.2 | V S | 11.2 | |
| 1 1̄ 0 | 9.95 | V S | 10.2 | |
| 2 0 0 | 8.23 | S | 8.26 | |
| 2 1 0 | 7.47 | m | | — |
| 0 2 0 | 6.85 | S | 6.89 | |
| 1 2 0 | 6.62 | W | | — |
| 3 0 0 | 5.49 | m s | | |
| 3 1̄ 0 | 4.90 | S | 4.97 | |
| 1 3 0 | 4.54 | m | 4.56 | |
| 2 3 0 | 4.22 | W | 4.26 | |
| 3 3 0 | 3.74 | W | 3.78 | |

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